

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 March 2004 (04.03.2004)

PCT

(10) International Publication Number
WO 2004/018359 A1

(51) International Patent Classification⁷: **C01B 33/149**

(21) International Application Number:
PCT/EP2003/008333

(22) International Filing Date: 29 July 2003 (29.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
102 38 463.0 22 August 2002 (22.08.2002) DE

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, UZ, VC, VN, YU, ZA, ZM, ZW.

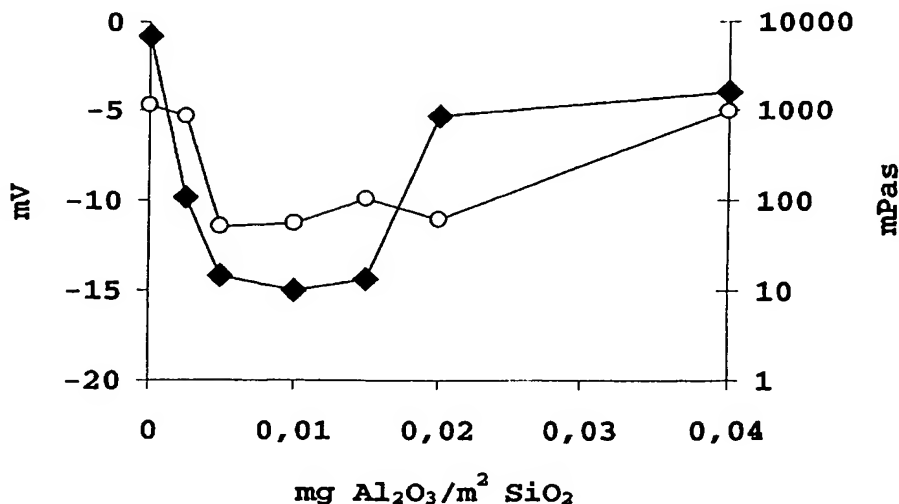
(84) Designated States (*regional*): Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

Declaration under Rule 4.17:

— as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO,
RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ,
UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, Eurasian patent

[Continued on next page]

(54) Title: STABILIZED, AQUEOUS SILICON DIOXIDE DISPERSION



(57) Abstract: Aqueous dispersion containing silicon dioxide powder, which is stable in a pH range of 2 to 6, which contains a cation-providing compound that is at least partially soluble in this pH range and the zeta potential of which is less than or equal to zero. It is produced by bringing silicon dioxide powder and at least one cation-providing compound into contact whilst moving in an aqueous medium. The dispersion can be used for chemical-mechanical polishing of metal surfaces.

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(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent
(AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB,
GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR)

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

Published:

— with international search report

Stabilized, aqueous silicon dioxide dispersion

The invention relates to an aqueous dispersion containing silicon dioxide, which is stable in the acid pH range, its production and use. The invention further relates to a
5 powder that can be used to produce the dispersion.

Silicon dioxide dispersions are generally not stable in the acid pH range. A possibility for stabilizing such dispersions is offered for example by the addition of aluminium compounds.

10 WO 00/20221 discloses an aqueous silicon dioxide solution that is stable in the acid range. It is produced by bringing silicon dioxide particles into contact with aluminium compounds in an aqueous medium. The quantity of aluminium compound required to produce the dispersion
15 claimed in the '221 application can be tracked by increasing the zeta potential and is achieved at the point where the rise in the zeta potential curve moves towards zero or a plateau is reached. The '221 application also claims dispersions in which the zeta potential achieves
20 only 50% of the maximum achievable value. In every case, the zeta potential of the claimed dispersions has strongly positive values of up to 30 mV. This means that the originally negatively-charged silicon dioxide particles have been completely cationized by the addition of the
25 aluminium compound. Although the claimed dispersion has good stability, it is no longer a silicon dioxide dispersion as the surface is covered with positively-charged aluminium species. This is a disadvantage in applications in which the dispersion is brought into
30 contact with anionic substances or dispersions. This can lead, for example, to unwanted flocculation or sedimentation.

US 2,892,797 on the other hand, discloses an aqueous silicon dioxide dispersion, which is stabilized by

treatment with an alkali metalate. Sodium aluminate is preferred in particular. Stabilization takes place through the anion, for example $[\text{Al}(\text{OH})_4]^-$. The dispersions are normally stable in a pH range of 5 to 9. The zeta potential of the powder thus treated is negative. The subsequent removal of the cation, by ion exchange processes for example, can be a disadvantage of this process. For special applications, such as for example chemical-mechanical polishing, alkali cations are generally undesirable. A further disadvantage is the low stability in more acid media below pH 5.

The object of the invention is to provide a silicon dioxide dispersion that is stable in the acid range, without changing the properties of the silicon dioxide powder by reversing the charge on the particle surface.

The invention provides an aqueous dispersion containing silicon dioxide powder with a silicon dioxide content of 10 to 60 wt.%, wherein

- the dispersion is stable in a pH range of 2 to 6,
- the dispersion additionally contains at least one compound, which is at least partially soluble in aqueous solution in the pH range 2 to 6 in the form of polyvalent cations, the cations being stable in a silicate-like environment as an anionic component of the particle surface of the silicon dioxide powder,
- the quantity of cation-providing compound in relation to the surface of the silicon dioxide is 0.001 to 0.1 mg cation-providing compound/m² silicon dioxide surface, the cation-providing compound being calculated as oxide and
- the zeta potential of the dispersion has values of less than or equal to zero.

The zeta potential is the outwardly-active potential of the particles and represents a measure of the electrostatic interaction between individual particles. It plays a part in the stabilization of suspensions and in particular of
5 dispersions containing dispersed, ultra-fine particles. The zeta potential can be determined, for example, by measuring the colloidal vibration current (CVI) of the dispersion or determining its electrophoretic mobility.

Cation-providing compounds according to the invention are
10 understood always to be those that are at least partially soluble in aqueous solution in the pH range 2 to 6 in the form of polyvalent cations, these cations being stable in a silicate-like environment as an anionic centre. These are compounds having Ca, Sr, Ba, Be, Mg, Zn, Mn, Ni, Co, Sn,
15 Pb, Fe, Cr, Al, Sc, Ce, Ti and Zr as cation.

A silicate-like environment is understood to mean that the cations of the above-mentioned metals are present in the form of metal-oxygen bonds with the silicon atoms of the silicon dioxide surface. They can also replace silicon
20 atoms in the silicon dioxide structure.

An anionic component is understood to be a component, which does not change the negative charge of the surface of a silicon dioxide powder, measured as zeta potential, or which shifts it towards more negative values.

25 Stable is understood to mean that the particles of the silicon dioxide powder do not agglomerate further in the dispersion and the viscosity of the dispersion does not change or changes only slightly (increase in viscosity of less than 10%) within a period of at least one week.

30 Preferred cation-providing compounds are amphoteric compounds with Be, Zn, Al, Pb, Fe or Ti as cation and mixtures of these compounds.

Amphoteric compounds are those that, at a given pH, act as a base in relation to a stronger acid and as an acid in relation to a stronger base.

Cation-providing compounds preferred in particular are
5 aluminium compounds, such as for example aluminium
chloride, aluminium hydroxychlorides of the general formula
 $\text{Al}(\text{OH})_x\text{Cl}$ in which $x=2-8$, aluminium chlorate, aluminium
sulfate, aluminium nitrate, aluminium hydroxynitrates of
the general formula $\text{Al}(\text{OH})_x\text{NO}_3$ in which $x=2-8$, aluminium
10 acetate, alums such as aluminium potassium sulfate or
aluminium ammonium sulfate, aluminium formiate, aluminium
lactate, aluminium oxide, aluminium hydroxide acetate,
aluminium isopropylate, aluminium hydroxide, aluminium
silicates and mixtures thereof. Aluminium silicate can, for
15 example, be Sipernat 820 A from Degussa AG, which is a
fine-particle aluminium silicate containing ca 9.5 wt.%
aluminium as Al_2O_3 and ca 8 wt.% sodium as Na_2O , or a sodium
aluminium silicate in the form of a zeolite A.

There is no restriction on the type of silicion dioxide
20 powder in the dispersion according to the invention. Thus
silicon dioxide powders produced by sol-gel processes,
precipitation processes or pyrogenic processes can be used.
It can be a metal oxide powder completely or partially
encased in silicon dioxide, provided that its zeta
25 potential is equal to or less than zero in the pH range
2 to 6.

Pyrogenically-produced silicion dioxide powder is
preferred.

Pyrogenically according to the invention is understood to
30 mean the formation of silicon dioxide by flame hydrolysis
of a compound or compounds containing silicon in the gas
phase in a flame produced by the reaction of a combustion
gas and an oxygen-containing gas, preferably air. Suitable
silicon-containing compounds are for example silicon
35 tetrachloride, methyltrichlorosilane, ethyltrichlorosilane,

propyltrichlorosilane, dimethyldichlorosilane, alkoxy-
silanes and mixtures thereof. Silicon tetrachloride
is preferred in particular. Suitable combustion gases are
hydrogen, methane, ethane, propane, hydrogen being
5 preferred in particular. During flame hydrolysis, highly-
disperse, non-porous primary particles are formed first,
which grow together as the reaction progresses to form
aggregates, which can further combine to form agglomerates.
The surface of the pyrogenically-produced silicon dioxide
10 particles has silanol groups (Si-OH) and siloxane groups
(Si-O-Si).

Pyrogenically-produced silicon dioxide powders also include
doped silicon dioxide powders and pyrogenically-produced
silicon-metal mixed oxide powders, provided that their zeta
15 potential is less than or equal to zero in the pH range
2 to 6.

The production of doped powders is disclosed for example in
DE-A-196 50 500. Typical doping components are for example
aluminium, potassium, sodium or lithium. The content of the
20 doping component is generally no greater than 1 wt. %.

Pyrogenically-produced mixed oxide powders are understood
to mean those in which both precursors of the mixed oxide
are hydrolyzed together in the flame. Typical mixed oxide
powders are silicon-aluminium mixed oxides or silicon-
25 titanium mixed oxides.

According to a particular embodiment, the ratio of the
cation-providing compound to the surface of the silicon
dioxide is preferably 0.0025 to 0.04, and in particular
0.005 to 0.02 mg cation-providing compound/m² silicon
30 dioxide surface.

The silicon dioxide surface corresponds to the specific
surface area of the silicon dioxide powder determined
according to DIN 66131. The BET specific surface area can

be 5 to 600 m²/g, the range 30 to 400 m²/g being preferred and the range 50 to 300 m²/g being preferred in particular.

The pH value of the dispersion according to the invention is 2 to 6. It is preferably 3 to 5.5. In particular, at a
5 BET specific surface area of the silicon dioxide powder of up to 50 m²/g it can be 3 to 4, at a BET specific surface area of 50 to 100 m²/g it can be 3.5 to 4.5, at a BET specific surface area of 100 to 200 m²/g 4 to 5 and at a BET specific surface area of more than 200 m²/g 4.5 to 5.5.

10 The pH value can, if necessary, be set using acids or bases. Preferred acids are hydrochloric acid, sulfuric acid, nitric acid or carboxylic acids, such as for example acetic acid, oxalic acid or citric acid. Preferred bases
15 are alkali hydroxides, such as KOH or NaOH, ammonia, ammonium salts or amines. If necessary, buffer systems can be formed by adding salts.

According to a particular embodiment, at a shear energy of 1.28 s⁻¹, the viscosity of the dispersion according to the invention can be at least 10% lower than the viscosity of a
20 dispersion of the same composition, which does not, however, contain a cation-providing compound. The viscosity is preferably 25%, in particular 50%, lower than that of a dispersion of the same composition, which does not, however, contain a cation-providing compound.

25 According to a particular embodiment, the number of agglomerates over 1 µm in size in the dispersion according to the invention can be at least 50% lower than the number in a dispersion of the same composition, which does not, however, contain a cation-providing compound. The number of
30 agglomerates over 1 µm in size is preferably 75%, in particular 90%, lower than in a dispersion of the same composition, which does not, however, contain a cation-providing compound.

The dispersion according to the invention can further contain preservatives. Suitable preservatives are, for example, benzylalcohol mono(poly)hemiformal, tetramethylolacetylenediurea, formamide monomethylol, trimethylolurea, N-hydroxymethylformamide, 2-bromo-2-nitropropane-1,3-diol, 1,6-dihydroxy-2,5-dioxahexane, chloromethylisothiazolinone, orthophenylphenol, chloroacetamide, sodium benzoate, octylisothiazolone, propiconazol, iodopropinyl butylcarbamate, methoxycarbonyl aminobenzimidazole, 1,3,5-triazine derivatives, methylisothiazolinone, benzoisothiazolinone and mixtures of these.

The invention further provides a process for the production of the dispersion according to the invention, wherein the silicon dioxide powder and at least one cation-providing compound in a quantity of 0.001 to 0.1 mg cation-providing compound/m² silicon dioxide surface are brought into contact whilst moving in an aqueous solution.

Bringing into contact whilst moving is understood to mean, for example, stirring or dispersing. Dissolvers, toothed gear disks, rotor-stator machines, ball mills or mechanically agitated ball mills, for example, are suitable for dispersal. Higher energy inputs are possible with a planetary kneader/mixer. However the effectiveness of this system depends on the mixture processed having a sufficiently high viscosity to incorporate the high shear energies required to disperse the particles. High-pressure homogenizers can be used to obtain aqueous dispersions with aggregate sizes in the dispersion of less than 200 nm.

With these devices at least two pre-dispersed suspension streams under high pressure are released through a nozzle. The two dispersion jets collide with each other exactly and the particles mill themselves. In another embodiment the pre-dispersion is also placed under high pressure, but the collision of the particles takes place against armoured

areas of wall. The operation can be repeated as often as desired to obtain smaller particles.

The process for the production of the dispersion according to the invention can be carried out in such a way that the
5 cation-providing compound, in solid form or as an aqueous solution, is added to an aqueous dispersion of silicon dioxide.

It can also be carried out in such a way that the silicon dioxide powder is added to an aqueous solution of the
10 cation-providing compound at once or in portions.

Furthermore, it is possible to add the silicon dioxide powder and the cation-providing compound to the liquid dispersion phase at the same time, in portions or continuously.

15 In this case, "at the same time" is understood to mean that the silicon dioxide powder and the cation-providing compound can be pre-mixed in the form of a physical or chemical mixture.

The invention further provides a powder of this type,
20 containing at least one cation-providing compound and silicon dioxide powder, the content of cation-providing compound, calculated as oxide, being 0.001 to 0.1 mg cation-providing compound/m² silicon dioxide surface.

Included in this are typical impurities of the starting
25 materials and impurities introduced during production. The content of impurities is less than 1 wt.%, and normally less than 0.1 wt.%.

The cation-providing compound is preferably an aluminium compound and the silicon dioxide a pyrogenically-produced
30 silicon dioxide powder.

The powder according to the invention can be incorporated rapidly into aqueous media.

In the simplest case, it can be produced by physical mixing of silicon dioxide powder and at least one cation-providing compound. Here it is useful to use individual packages completely. Consequently it is not necessary to have
5 present a homogeneous distribution of silicon dioxide and cation-providing compound.

The powder according to the invention can further be obtained also by spraying onto the silicon dioxide powder at least one compound that is soluble in the pH range of <6
10 or that provides cations by chemical reaction in the pH range <6. The solution of the cation-providing compound can be sprayed on in heated mixers and dryers with spray devices, either continuously or in batches. Suitable
15 devices are, for example: plough mixers, disk- or fluidized bed dryers.

The solution of the cation-providing compound can be sprayed on with an ultrasound nozzle or atomized. The mixer can optionally also be heated.

Furthermore, the powder according to the invention can be
20 obtained by separating a cation-providing compound, for example aluminium chloride, from vapour in a fluidized bed or mixer.

The invention further provides the use of the dispersion according to the invention for chemical-mechanical
25 polishing of metal surfaces, in particular polishing of copper surfaces, for the production of ink-jet papers, for gel batteries, for clarifying/fining wine and fruit juices, for water-based dispersion paints to improve the suspension behaviour of pigments and fillers and to increase scratch-
30 resistance, to improve the stability and "blackness" of carbon black dispersions for ink-jet inks, to stabilize emulsions and dispersions in the field of biocides, as a reinforcing agent for natural latex and synthetic latexes, to produce latex/rubber articles such as gloves, condoms,
35 infant soothers or foamed rubber, in the sol-gel field, to

remove surface stickiness (anti-blocking), to achieve an anti-slip effect in paper and cardboard, to improve slip resistance, to produce optical fibres, to produce quartz glass.

- 5 It is surprising that a silicon dioxide dispersion brought into contact with a cation-providing compound has good stability in the acid range and at the same time the surface of the silicon dioxide particle retains, or even strengthens, its negative surface charge.
- 10 The mechanism of this stabilization has not yet been explained. However, it must differ from that disclosed in WO 00/20221. Here, the charge of silicon dioxide particles is completely reversed by positively-charged aluminium species, giving the particles a positively-charged shell.
- 15 The mechanism must also differ from that disclosed in US 2,892,797. Here, a negatively-charged metalate ion is incorporated into the surface of a silicon dioxide particle. Although the particles thus changed, like the particles in the dispersion according to the invention,
20 have a negative surface charge, they have little stability in the acid pH range.

Examples

Analysis methods

The zeta potential is determined with a DT-1200 type device from Dispersion Technology Inc., by the CVI method.

- 5 The viscosity of the dispersions was determined with a Physica MCR 300 rotation rheometer and CC 27 measuring beaker, measurement taking place at shearing rates of 0.01 to 500 s⁻¹ and 23°C. The viscosity is given at a shearing rate of 1.28 s⁻¹. This shearing rate lies in a range in
10 which structurally viscous effects have a clear impact.

The particle/agglomerate sizes were determined with Horiba LB 500 and LA 300 devices, or a Malvern Zetasizer 3000 Hsa.

Dispersal

- 15 The dispersion devices used were, for example, a Dispermat AE-3M type dissolver from VMA-GETZMANN with a dissolver disk diameter of 80 mm or an Ultra-Turrax T 50 type rotor/stator dispersing unit from IKA-WERKE with S50N - G45G dispersing tools. When using rotor-stator devices, the charge container is cooled to room temperature.
- 20 Dispersal can also be carried out using a high-energy mill. For charges containing 50 kg silicon dioxide powder each, a portion of the DI water is placed into a 60 l special steel charge container. The corresponding quantity of Aerosil powder is sucked in using an Ystrahl Conti-TDS 3 dispersion
25 and suction mixer and roughly pre-dispersed. During powder intake, a pH value of 3.5 +/- 0.3 is maintained by adding sodium hydroxide solution and aluminium chloride solution. After powder intake, dispersion is completed with the Conti TDS 3 (stator slit width of 4 mm) with a closed suction
30 nozzle at maximum speed. Before rotor/stator dispersal the pH of the dispersion was set at 3.5 by adding more sodium hydroxide solution and this remained the same after

dispersing for 15 minutes. By adding the remaining quantity of water, an SiO₂ concentration of 20 wt.% was set. This pre-dispersion is milled in an HJP-25050 Ultimaizer System high-energy mill from Sugino Machine Ltd., at a pressure of 250 Mpa and a diamond nozzle diameter of 0.3 mm and two passes through the mill.

Chemicals

- The aerosil types 50,90,200 and 300 from Degussa AG were used as the silicon dioxide powder. AlCl₃ in the form of the hexahydrate was used as the water-soluble aluminium compound. A 1 wt.% solution, in relation to Al₂O₃, was used to simplify dosing and homogenization. A 1 N NaOH solution or a 1 N HCL solution was used to correct the pH.
- To allow comparisons between the viscosity of the dispersions, a uniform pH value of 3.5 is optionally set by adding a further 1 N NaOH.

Dispersions

- The various charge sizes and the properties of the dispersions obtained are given in Tables 1 and 2.

Example 1a (Reference example)

- 100 g Aerosil 50 (BET specific surface area ca 50 m²/g) were incorporated in portions into 385 g DI water using a dissolver at a setting of ca 1800 rpm. This produced a pH value of 3.5. The remaining 15 g DI water were then added to achieve a 20 percent dispersion and this was then dispersed for 15 minutes at 2000 rpm and 15 minutes using an Ultra Turrax at ca 5000 rpm.

Examples 1b-g

100 g Aerosil 50 were incorporated in portions into 385 g DI water and 1.25 g of a 1 wt.% aqueous aluminium chloride solution (in relation to aluminium oxide), using a
5 dissolver at a setting of ca 1800 rpm. This produced a pH value of 3.4, which was set at pH 3.5 by adding 0.7 g 1N NaOH. The remaining 13.1 g water were then added to achieve a 20 wt.% dispersion and this was then dispersed for 15 minutes at 2000 rpm and 15 minutes with an Ultra Turrax at
10 ca 5000 rpm.

Examples 1c-g were carried out in the same way as 1b.

Example 2a (Reference example)

100 g Aerosil 90 were incorporated in portions into 370 g
15 DI water using a dissolver at a setting of ca 1800 rpm and were then dispersed for 15 minutes at 2000 rpm. The pH value was then set at 3.5 using 1N HCl and the dispersion was dispersed for 15 minutes with an Ultra Turrax at ca 5000 rpm. The remaining water was then added to achieve a
20 20 wt.% dispersion and the pH value was re-set to 3.5.

Example 2b

100 g Aerosil 90 were incorporated alternately, in portions, into 370 g DI water using a dissolver at a setting of ca 1800 rpm and then dispersed at a setting of
25 ca 2000 rpm. 2.50 g of a 1 wt.% solution (in relation to aluminium oxide) of aluminium chloride were then added whilst dispersing with an Ultra Turrax at ca 5000 rpm and this was dispersed for 15 minutes. 26.3 g DI water and 1.24 g 1N NaOH were then added to obtain a 20 wt.%
30 dispersion with a pH value of 3.5.

Example 3a (Reference example)

250 g DI water and 20 g of a 1 wt.% aqueous aluminium chloride solution (in relation to aluminium oxide) were provided. Aerosil 90 was added in portions using a
5 dissolver. The pH value was maintained at 3.5 during this process. After adding ca 40 g Aerosil 90 powder, the dispersion thickened very strongly making further additions impossible.

Examples 3b, 3c

- 10 100 g Aerosil 90 were incorporated into 250 g DI water using a dissolver and 10 g of a 1 wt.% aqueous aluminium chloride solution (in relation to aluminium oxide) and 1N NaOH were added alternately in portions so that the pH value was 3.3 to 4.2. A further 100 g Aerosil 90 and a
15 further 10 g of a 1 wt.% aluminium chloride solution (in relation to aluminium oxide) and sufficient 1N NaOH were then added alternately in portions using an Ultra-Turrax at 5000 rpm to produce a pH value of 3.5 at the end of addition.
- 20 In example 3c a pH value of 4.0 was set.

Example 4 (Reference example)

- 50 g Aerosil 90 were incorporated in portions into 350 g DI water using a dissolver at a setting of ca 1800 rpm and
25 were then dispersed for 15 minutes at 2000 rpm. 100 g of a 1 wt.% solution (in relation to aluminium oxide) of aluminium chloride were then added whilst dispersing in an Ultra Turrax at ca 5000 rpm and dispersed for 15 minutes and the pH value of 2 was increased to a pH of 3.5 using
30 30% sodium hydroxide solution.

Examples 5

Example 5a was carried out in the same way as 2a. Examples 5b-d were carried out in the same way as 2b. For examples

5e-g, ca 100 ml of the dispersion of example 5d was brought up to the pH value given in Table 2 with 30% sodium hydroxide solution added drop-wise, homogenized for ca 5 minutes with a magnetic stirrer and the zeta potential of each was measured.

Examples 6

Example 6a was carried out in the same way as 2a. Examples 6b-d were carried out in the same way as 2b.

10 **Fig. 1** shows the zeta potential in mV (♦) and the viscosity in mPas (o) of examples 1a-g as a function of mg Al₂O₃/m² SiO₂-surface.

Example 7 - Powder production

500g silicon dioxide powder (Aerosil 200, Degussa) were added to a 20 l Lodige mixer. 20g of a 5 wt.% (in relation to Al_2O_3) aluminium chloride solution with a spray output of ca 100 ml/h were applied at a speed of 250 rpm within 10-15 min. The powder has 0.01mg $\text{Al}_2\text{O}_3/\text{m}^2$ silicon dioxide surface, a BET specific surface area of 202 m^2/g and a tamped density of ca 60 g/l. The water content is ca 4% and can, if desired, be reduced by heating the wiper or by subsequent drying in a drying cabinet, revolving tube or fluidized bed. An aqueous dispersion (20 wt.-%) has a pH value of 2.6.

Table 1: Aqueous Aerosil dispersions⁽¹⁾

Example	BET SiO ₂	Al ₂ O ₃ ⁽²⁾	DI-H ₂ O provided	Total DI-H ₂ O	1N NaOH
	[m ² /g]	[mg]	[g]	[g]	[g]
1a	50	0	375	400	-
1b	50	12.5	375	398.1	0.7
1c	50	25	375	395.8	1.7
1d	50	50	375	393.1	1.9
1e	50	75	375	389.1	2.0
1f	50	100	375	387.9	2.1
1g	50	200	375	376.8	2.5
2a	90	0	370	399.8	0.2 ⁽³⁾
2b	90	25	370	396.3	1.2
2c	90	100	370	385.0	5.0
2d	90	200	370	370.9	9.1
3a	90	200	250	-	-
3b	90	200	250	268.8	11.2
3c	90	200	250	268.3	11.7
4	90	1000	350	-	7 ⁴⁾
5a	200	0	360	399.9	0.1 ⁽³⁾
5b	200	25	360	396.0	1.5
5c	200	100	360	382.9	7.1
5d	200	200	360	367.2	12.8
5e	200	200	360	367.2	12.5 ⁵⁾
5f	200	200	360	367.2	12.5 ⁵⁾
5g	200	200	360	367.2	12.5 ⁵⁾
6a	300	0	330	399.8	0.2 ⁽³⁾
6b	300	200	330	368.6	11.4
6c	300	300	330	352.0	18.0
6d	300	400	330	331.2	28.8

1) in all trials 100 g SiO₂ each, except 3: 200 g and 4: 50 g; Ex. 1: Aerosil 50, Ex. 2,3,4: Aerosil 90, Ex. 5: Aerosil 200, Ex.6: Aerosil 300, all Degussa AG;

2) Al₂O₃ used as AlCl₃;

3) 1N HCl instead of 1N NaOH;

4) 30% sodium hydroxide solution;

5) additionally a few drops of 30% sodium hydroxide solution to achieve the corresponding pH value in Table 2.

Table 2: Analytical data of the dispersions⁽¹⁾

Example	SiO ₂ Content	Al ₂ O ₃ /SiO ₂	pH of Dispersion	Zeta- Potential	Visco- sity ⁽²⁾
	[wt. %]	[mg/m ²]		[mV]	[mPas]
1a	20	0	3.6	-0.8	1142
1b	20	0.0025	3.5	-9.8	846
1c	20	0.0050	3.4	-14.2	50
1d	20	0.0100	3.3	-15.0	55
1e	20	0.0150	3.4	-14.4	104
1f	20	0.0200	3.0	-5.3	60
1g	20	0.0400	3.1	-3.9	970
2a	20	0	3.3	-0.5	246
2b	20	0.0028	3.2	-10.0	95
2c	20	0.0111	3.1	-9.9	40
2d	20	0.0222	3.0	-6.5	82
3a	⁽³⁾	0.0111	-	-	-
3b	40	0.0111	3.2	-11.4	205
3c	40	0.0111	4.0	-13.3	n.d. ⁽⁴⁾
4	10	0.222	3.3	+ 25	n.d.
5a	20	0	3.5 3	-0.4 3	⁽⁵⁾
5b	20	0.0013	3.4	-4.1	1080
5c	20	0.0050	3.0	-6.2	672
5d	20	0.0100	3.1	-6.3	864
5e	20	0.0100	3.4	-7.75	n.d.
5f	20	0.0100	5.0	-9.5	n.d.
5g	20	0.0100	6.0	-11.3	n.d.
6a	20	0	-	-	(5)
6b	20	0.0067	3.3	-6.6	1520
6c	20	0.0100	3.3	-6.7	537
6d	20	0.0133	3.4	-5.2	1160

- 5 1) measured after one week;
 2) shearing rate of 1.28 s⁻¹;
 3) no 40 percent dispersion could be produced;
 4) n.d. = not determined;
 5) dispersion gelled

Claims:

1. An aqueous dispersion containing silicon dioxide powder with a silicon dioxide content of 10 to 60 wt.%, wherein
the dispersion is stable in a pH range of 2 to 6,
5 the dispersion additionally contains at least one compound, which is at least partially soluble in aqueous solution in the pH range 2 to 6 in the form of polyvalent cations, these being stable in a silicate-like environment as an anionic component
10 of the particle surface of the silicon dioxide powder,
the quantity of cation-providing compound in relation to the surface of the silicon dioxide is 0.001 to 0.1 mg cation-providing compound/m² silicon
15 dioxide surface, the cation-providing compound being calculated as oxide and
the zeta potential of the dispersion has values of less than or equal to zero.
2. An aqueous dispersion as claimed in claim 1, wherein
20 the cation-providing compound includes an amphoteric compound with Be, Zn, Al, Pb, Fe or Ti as cation, and mixtures of these compounds.
3. An aqueous dispersion as claimed in claim 2, wherein the amphoteric compound is an aluminium compound.
- 25 4. An aqueous dispersion as claimed in claims 1 to 3, wherein the silicon dioxide powder is a pyrogenically-produced silicon dioxide powder.
5. An aqueous dispersion as claimed in claim 4, wherein the BET specific surface area is 5 to 600 m²/g.

6. An aqueous dispersion as claimed in claims 1 to 5,
wherein the pH value is 3 to 5.
7. An aqueous dispersion as claimed in claims 1 to 6,
wherein acids, preferably hydrochloric acid, sulfuric
5 acid, nitric acid, C1-C4 carboxylic acids or bases,
preferably alkali hydroxides, ammonia, ammonium salts
or amines are used to regulate the pH value.
8. An aqueous dispersion as claimed in claims 1 to 7,
wherein the viscosity at a shear energy of 1.28 s^{-1} is
10 at least 10% lower than the viscosity of a dispersion
of the same composition that contains no cation-
providing compound.
9. An aqueous dispersion as claimed in claims 1 to 8,
wherein the number of agglomerates with a size greater
15 than $1 \mu\text{m}$ is at least 50% lower than that of a
dispersion of the same composition that contains no
cation-providing compound.
10. An aqueous dispersion as claimed in claims 1 to 9,
wherein the average secondary particle size of the
20 silicon dioxide powder is less than 200 nm.
11. An aqueous dispersion as claimed in claims 1 to 10,
wherein it contains preservatives.
12. A process for the production of the aqueous dispersion
as claimed in claims 1 to 11, wherein silicon dioxide
25 powder and at least one cation-providing compound in a
quantity of 0.001 to 0.1 mg cation-providing compound/ m^2
silicon dioxide surface are brought into contact whilst
moving in an aqueous medium.
13. A process for the production of the aqueous dispersion
30 as claimed in claim 12, wherein the cation-providing
compound is added, in solid form or as an aqueous
solution, to an aqueous dispersion of silicon dioxide.

14. A process for the production of the aqueous dispersion as claimed in claim 12, wherein the silicon dioxide powder is added at once, or in portions to an aqueous solution of the cation-providing compound.
- 5 15. A process for the production of the aqueous dispersion as claimed in claim 12, wherein the silicon dioxide powder and cation-providing compound are added to the liquid dispersion phase at the same time, in portions or continuously.
- 10 16. A powder consisting of at least one cation-providing compound and silicon dioxide powder, the content of the cation-providing compound, calculated as oxide, being 0.001 to 0.1 mg cation-providing compound/m² silicon dioxide surface.
- 15 17. A powder as claimed in claim 16, wherein the cation-providing compound is an aluminium compound and the silicon dioxide is a pyrogenically-produced silicon dioxide powder.
- 20 18. Use of the dispersion as claimed in claims 1 to 11 for chemical-mechanical polishing of metal surfaces, in particular polishing of copper surfaces, for the production of ink-jet papers, for gel batteries, for clarifying/fining wine and fruit juices, for water-based dispersion paints to improve the suspension
- 25 behaviour of pigments and fillers and to increase scratch resistance, to improve the stability of the "black" of carbon black dispersions for ink-jet inks, to stabilize emulsions and dispersions in the field of biocides, as a reinforcing agent for natural latex and
- 30 synthetic latexes, in the sol-gel field, for removing surface stickiness (antiblocking) to achieve an antislip effect in paper and cardboard, to improve slip resistance, to produce optical fibres and to produce quartz glass.

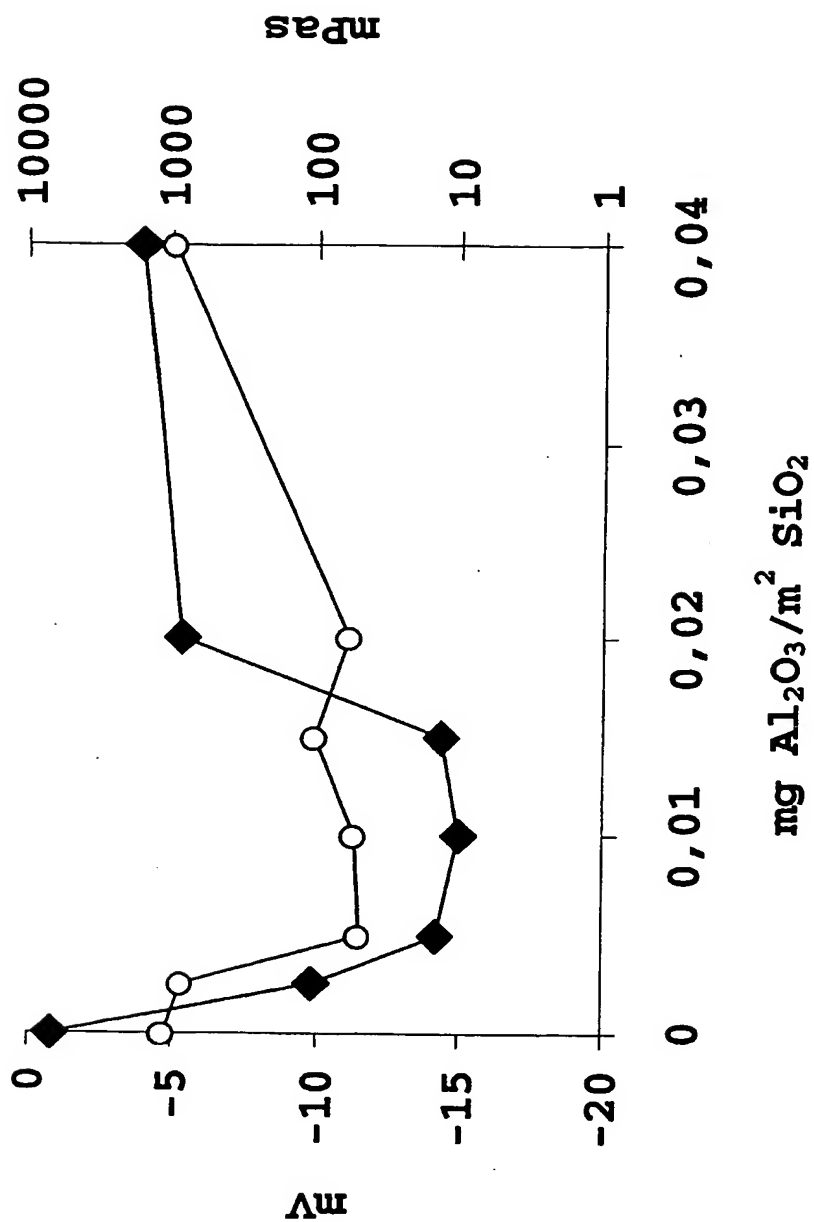


Fig. 1

INTERNATIONAL SEARCH REPORT

Int. Application No

PC1/EP 03/08333

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B33/149

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 20221 A (CABOT CORP) 13 April 2000 (2000-04-13) cited in the application page 3, line 11-30 page 11, line 3-35 page 25, line 35 -page 26, line 8 figure 1; example 1	1-18
X	US 2 892 797 A (ALEXANDER GUY B ET AL) 30 June 1959 (1959-06-30) cited in the application the whole document	1-18
X	US 3 007 878 A (HENDRIK BOLT GERARD ET AL) 7 November 1961 (1961-11-07) column 1, line 11-52 column 3, line 42 -column 4, line 45 example 1	1-18
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 November 2003

Date of mailing of the international search report

14/11/2003

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INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/EP 03/08333

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 603 805 A (ANDERSSON KJELL ET AL) 18 February 1997 (1997-02-18) column 2, line 25-44 column 4, line 4-15 column 5, line 14-32 -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

Application No

PCT/EP 03/08333

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0020221	A	13-04-2000	AU 6281399 A EP 1124693 A1 JP 2002526564 T WO 0020221 A1 US 6420039 B1	26-04-2000 22-08-2001 20-08-2002 13-04-2000 16-07-2002
US 2892797	A	30-06-1959	NONE	
US 3007878	A	07-11-1961	NONE	
US 5603805	A	18-02-1997	SE 501214 C2 AT 138354 T AU 667966 B2 AU 4988193 A BR 9306878 A CA 2141551 A1 CN 1084490 A , B DE 69302823 D1 DK 656872 T3 EP 0656872 A1 ES 2087767 T3 FI 950622 A JP 2787377 B2 JP 8502016 T MX 9305272 A1 NO 950738 A NZ 255615 A RU 2081060 C1 SE 9202502 A WO 9405596 A1	12-12-1994 15-06-1996 18-04-1996 29-03-1994 08-12-1998 17-03-1994 30-03-1994 27-06-1996 07-10-1996 14-06-1995 16-07-1996 13-02-1995 13-08-1998 05-03-1996 28-02-1994 27-02-1995 27-11-1995 10-06-1997 01-03-1994 17-03-1994